THE MASS SPECTROMETER

by ALFRED O. C. NIER

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THE MASS SPECTROMETER

This sensitive instrument sorts atoms and molecules of various weights by means of a magnetic field. Developed by physicists, it is now widely utilized in other sciences and in technology

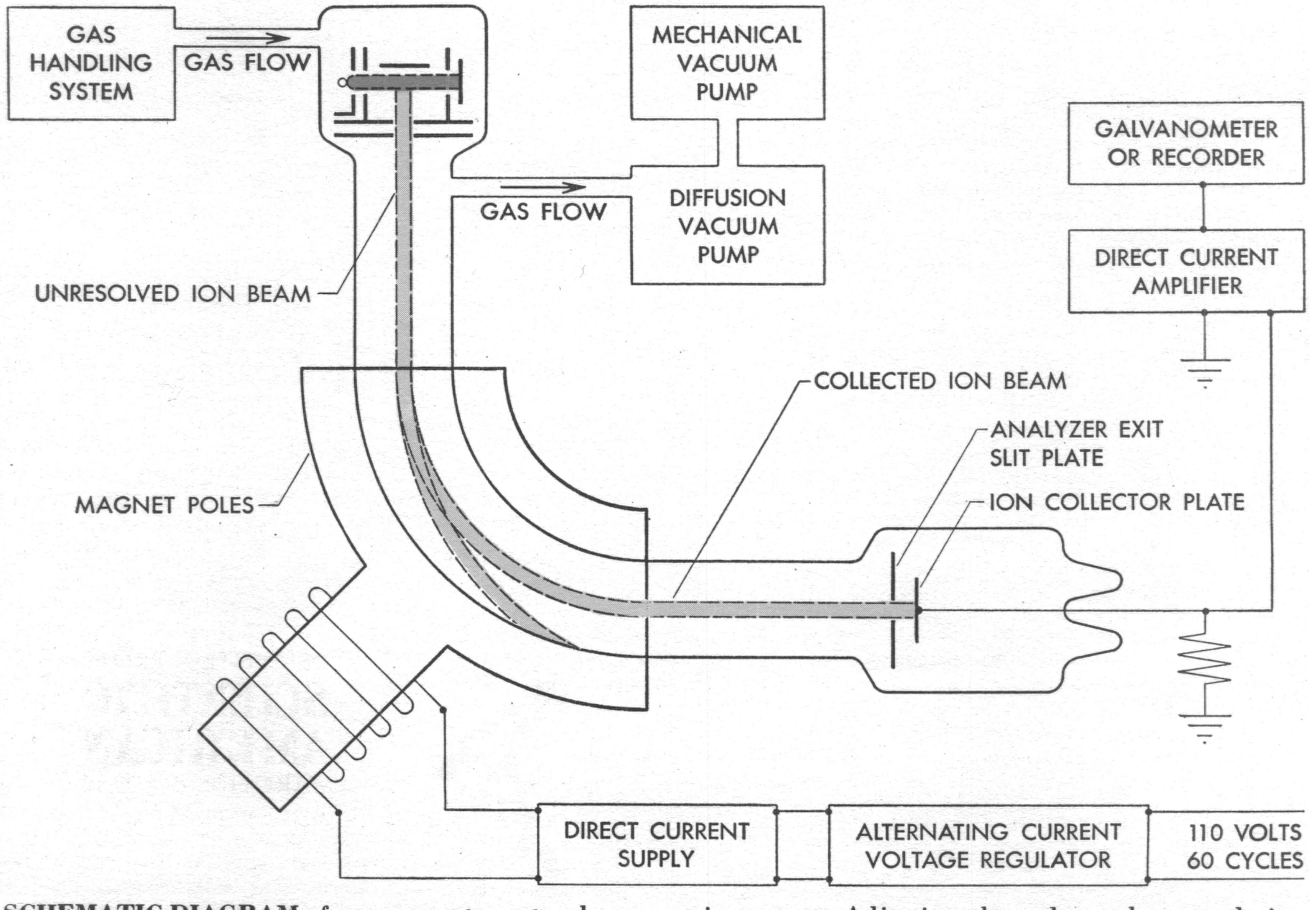
by Alfred O. C. Nier

THE MASS spectrometer is a classic example of the instrument that starts as a laboratory contrivance and becomes one of the great general tools of mankind. It grew out of the electrified glass tubes with which physicists liked to experiment in the late 1800s; today it is used as a research instrument in fields as widely diverse as chemistry, geology, biology and medicine, and is an indispensable piece of equipment in various industries. As recently as 1940 there were probably fewer than a dozen such instruments in operation in the world; now there are many hundreds, and their use steadily grows.

Basically the mass spectrometer is an instrument for sorting and identifying atoms or molecules. The particles are ionized (given an electric charge) and then fired across a magnetic field which bends their flight into a circular path. The heavier of two ions will fly in a wider arc than the lighter one and hit a different target. The instrument readily separates ions with very slight differences in weight. And since the speed of the particles, strength of the magnetic field and paths of flight are all accurately known, it is easy to calculate precisely the relative masses of the various ions.

A mass spectrometer sorts a mixed stream of ions by atomic weight just as a glass prism separates a beam of white light into a spectrum of its component colors or wavelengths of light. If the sorted ions are caught on a photographic plate, the apparatus is called a mass spectrograph; if they are detected and recorded by electrical means, it becomes a mass spectrometer.

The instrument can easily identify the



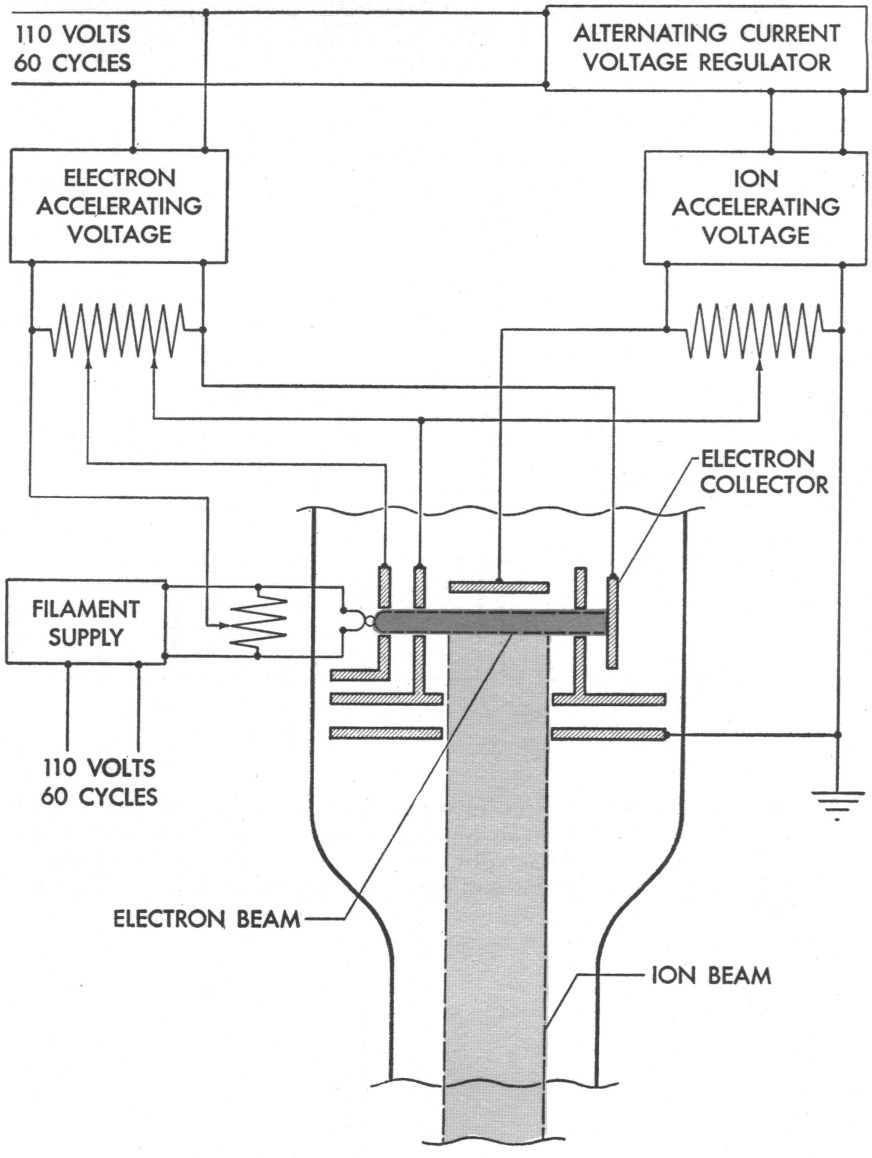
SCHEMATIC DIAGRAM of a mass spectrometer shows path of ions (*in color*). Those that reach the collector plate signal their presence by a minute electric current. Adjusting the voltage that speeds ions down the tube, or the magnetic field that bends their path, brings ions of desired weight to the collector.

ingredients of air or any other gas and offers almost unlimited possibilities as a gas analyzer. It can analyze solids when they are converted to the gaseous form.

In principle the mass spectrometer goes back, as do so many powerful instruments today, to humble beginnings in the observations of research workers in the latter part of the last century. Physicists then were greatly interested in the study of electrical discharges in gases. To perform these studies they used a glass bulb having a pair of sealed-in metal electrodes, called anode and cathode. When a high voltage was applied across the electrodes and pressure in the bulb was reduced by pumping out some of its air or gas, the remaining gas became a conductor and glowed like a neon sign. From observations of this glow came some of our most fundamental and now familiar concepts of the nature of matter.

CHIEF among these were the discoveries of J. J. Thomson, who in 1897 began a famous series of experiments. Investigating the then mysterious cathode rays, which streamed from the negatively charged cathode in such a tube, Thomson determined that they were made up of particles. The individual particles always had the same mass and electric charge, regardless of the gas used in the discharge tube. Thus he discovered the electron, the smallest particle of matter, and opened the electronic age. He then turned to the anode rays seemingly coming from the positively charged anode. These also, he demonstrated, were streams of particles, but in their case the mass of the particles depended on the atomic weight of the gas in the tube. (Actually his anode rays were positively charged ions—atoms or molecules stripped of an electron by collisions in the electrical discharge.) Thomson thereby contributed to the growing chain of evidence that led to the realization that all matter is composed of atoms and that the weights of the atoms are directly proportional to what chemists had long recognized as the relative combining weights of the elements.

Thomson passed the positively charged anode rays through suitable combinations of electric and magnetic fields and found that the rays could be separated according to mass as the ions of different weights were pulled into different paths by the field forces. And in further exploration of the atomic weights of elements by this means he made another discovery. Chemists, in setting up their atomic weight scale, had arbitrarily taken oxygen as 16. The relative weights of the other elements tended to be integers also. But there were well-known discrepancies from this whole-number rule. For example, the rare atmospheric gas neon had an atomic weight of 20.2. In 1912 Thomson put a bit of pure neon



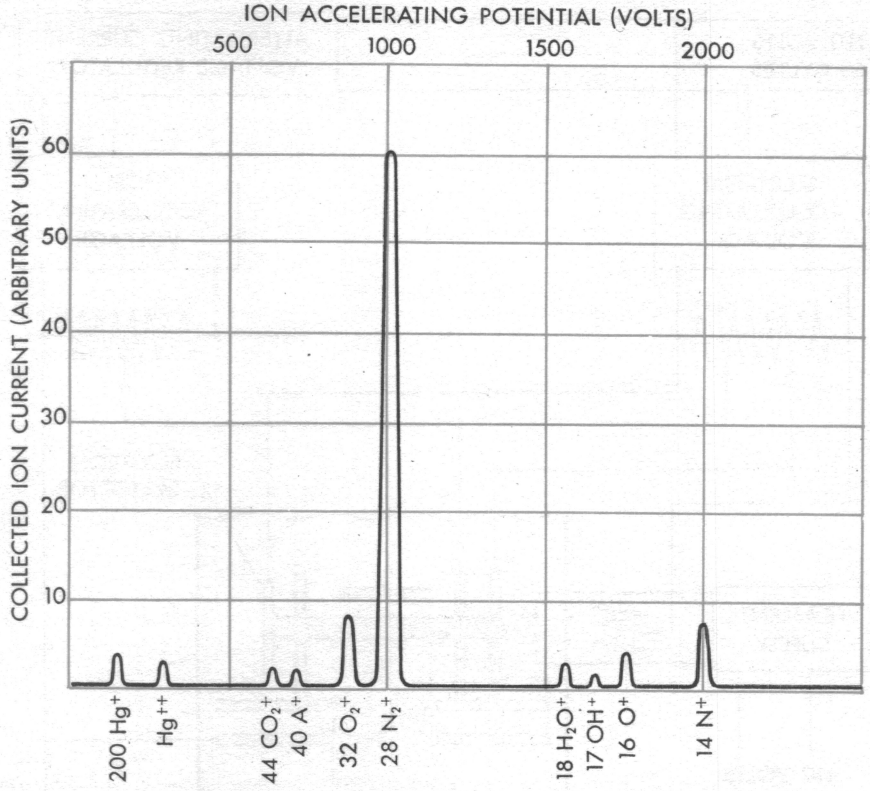
DETAIL OF ION SOURCE shows electron beam that ionizes the gas to be analyzed and the slotted electrodes through which the ion beam emerges. Voltages applied to the electrodes determine speeds of electrons and ions.

in his apparatus and found that it consisted of not one type of atom but two, some with a weight of 22, many more with a weight of 20, averaging out to 20.2. Thus he established the fact that some elements have isotopes—atoms of slightly different weight but the same chemical nature.

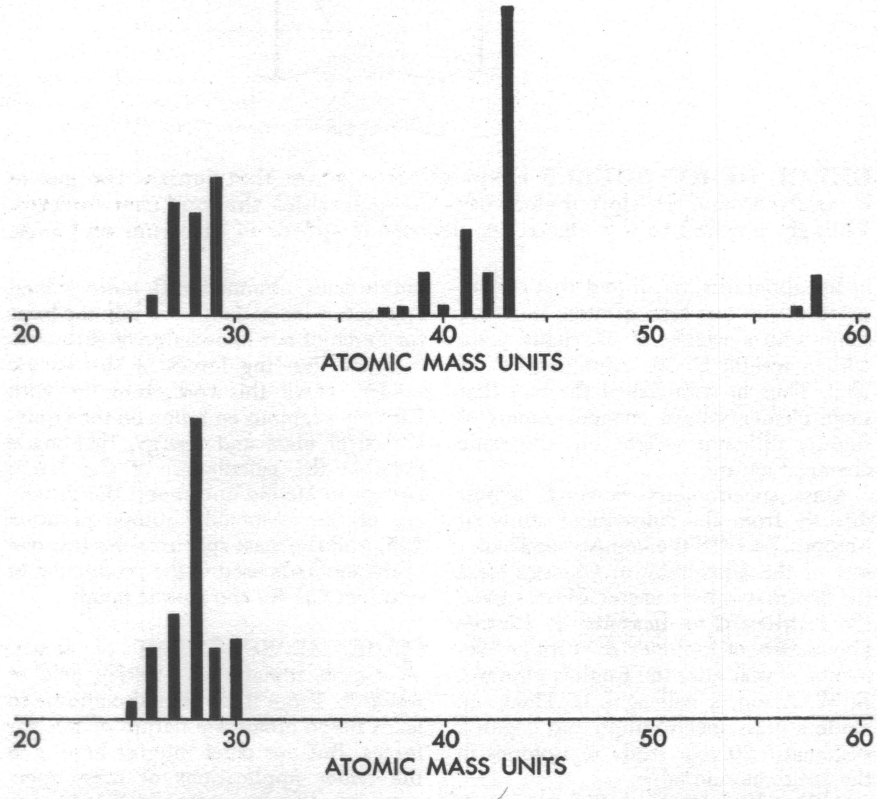
Mass spectrometry flowered almost directly from the subsequent study of isotopes. In 1918 the late Arthur Dempster of the University of Chicago built the first mass spectrometer. He designed the instrument to measure the relative abundance of isotopes in various elements. A year later the English physicist F. W. Aston, a colleague of Thomson, made a mass spectrograph and began a systematic 20-year study of isotopes in the entire atomic table.

Although many of Aston's measurements of minute deviations in atomic masses are now superseded by more accurate ones, obtained with more refined apparatus, his patient work laid the basis for much of our knowledge of the structure and binding forces of the atomic nucleus. It was this work, combined with Einstein's famous equation on the equivalence of mass and energy, that made possible the calculation of the latent energy in atomic nuclei and the discovery of the fissionable isotope uranium 235. And the mass spectrometer was one of the methods used in the production of uranium 235 for the atomic bomb.

THE MEASUREMENT of atomic masses remains an exciting field of research. From it we should continue to learn much about the nature of nuclear forces. But our chief interest here is in the wider applications of mass spectroscopy. By now it has enabled us to measure the relative abundance of most, if not all, of the isotopes occurring in



SPECTRUM OF AIR is plotted in terms of accelerating voltage required to focus each ion. The electron bombardment has not only ionized the various air molecules but has split some of them apart, as is shown by presence of monatomic oxygen and nitrogen. Mercury comes from pump.



HYDROCARBON SPECTRA for butane (*top*) and ethane (*bottom*) indicate relative abundance of molecular fragments after gas is broken up by electrons in spectrometer. Each pure hydrocarbon gives a unique picture.

nature and of those produced artificially in the laboratory. The study of isotopic abundances has many valuable applications in other fields of science besides physics. In addition, the mass spectroscope's convenience as an analyzing instrument makes it an important industrial tool.

In the early instruments the gas to be analyzed was ionized by bombardment with electrons from an electrical discharge. Most modern mass spectrometers produce ions by a more stable and controlled means. In the commonest type of instrument, the electrons stream from a hot tungsten wire and are accelerated through a potential difference of about 100 volts to give them the kinetic energy required to ionize the gas molecules. The gas is admitted continuously into the vacuum chamber of the instrument through a small "leak." The chamber is continuously pumped so that the net pressure is reduced to about one billionth of an atmosphere—a pressure so low that once an ion is formed there is little likelihood it will collide with another ion or gas molecule before it is caught on the detecting plate.

The ions are fired into the magnetic field at high speed. This is done in one form of the instrument by directing them through slits in a pair of parallel metal plates, across which an electrical potential difference is applied. Emerging from the slit in the second plate, the ions coast in straight lines until they pass between the poles of the magnet. The magnetic force, exerted at right angles to their direction of motion, causes the ions to curve in circular paths. The radius of curvature depends on the number of electrons lost in ionization (usually one), the difference in potential through which the ions fell, the strength of the magnetic field and the atomic weight of the ions being measured. By adjusting either the magnetic field or the difference in potential, ions of any particular weight can be made to hit a predetermined target. This is a slit behind which is mounted a plate. The ions impinging on this plate set up a tiny electric current, which is measured by special instruments.

ONE of the practical applications of the mass spectrometer is in the petroleum industry. Here the molecules to be analyzed are organic gases made up of many atoms. When struck by the electrons, such molecules are shattered into ionized fragments. For a given energy of bombarding electrons, these fragments may be made to give a mass spectrum characteristic of the gas bombarded, down to the actual arrangement of atoms in the molecule and the number and types of atoms present. Thus mass spectrometry can distinguish between two or more different chemical compounds having the same molecular

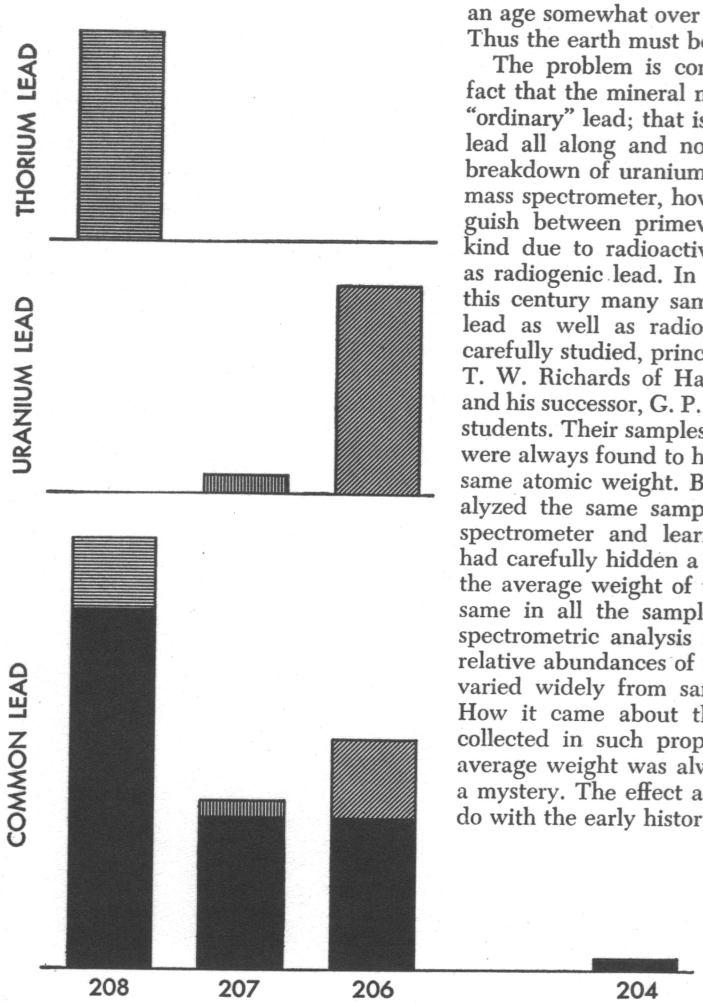
formula. This is extremely useful in the petroleum field, where many compounds are so nearly alike in properties that it is often difficult to identify them in a mixture by ordinary chemical means. Many oil refinery laboratories have set up spectrum patterns for hundreds of pure compounds and run routine analyses of mixtures having as many as several dozen components.

Such analyses are usually made in laboratories on samples brought to the instrument. But a mass spectrometer can also be put directly into the process stream in a continuous-flow chemical plant to provide a continuous analysis and automatic feedback control of the composition of the process stream. The first notable application of this kind was in the U-235 gaseous-diffusion plant at Oak Ridge, where the process stream is continuously monitored by a battery of strategically placed instruments for traces of air, refrigerants and other contaminants that may leak into the system. Each instrument is pretuned to the impurities being watched, just as a push-button radio is pretuned to certain stations. A clock and switch arrangement puts the instrument through its preset tests in sequence. Each analysis takes 24 seconds, and a single instrument can make 3,600 determinations a day, using small samples of gas which total altogether only two cubic centimeters. The amounts of the impurities are automatically recorded on a single chart, which allows an operator to see the entire chemical analysis of the stream at any time and note any changes that have taken place in it.

A portable mass spectrometer was developed to detect minute leaks in the system. The plant has miles of pipes, valves, vacuum pumps and vessels that must be kept tighter than those in any ordinary chemical plant. To have checked the completed plant for leaks by conventional means would have required about 1,000 test stations, each manned by a team working 8,000 hours to cover the million or so critical points in the system. With mass spectrometers acting as leak detectors the gigantic task was accomplished with only about 3 per cent of that effort. The plant was completed with great savings in time, materials and skilled manpower.

IN BIOLOGY the mass spectrometer has been useful for studying respiration, among other things. F. A. Hitchcock and his colleagues at Ohio State University have used a continuous-reading instrument to analyze the composition of respiratory gases under various conditions, including sudden changes in pressure. At the University of Minnesota Fletcher Miller and Allan Hemingway analyzed, with a special portable instrument, the rate of nitrogen elimination in patients suffering certain lung disorders, and other workers at the University have made continuous respiratory gas analyses during thoracic surgery. At the same institution the botanist Allan Brown and his students have examined metabolic gas exchanges in growing plants. Here the mass spectrometer follows continuously the composition of the gas surrounding the plants as the photosynthetic process takes place.

The mass spectrometer is an indispensable item of equipment in biological tracer experiments employing stable isotopes. For many investigations of metabolism stable isotopes are preferable to radioactive isotopes; for some they are the only ones available. For instance, nitrogen and oxygen, two important elements in biological studies, have no suitable radioactive isotopes but useful stable ones. The mass spectrometer can measure extremely small traces of an element; with it, for example, M. G. Inghram and his colleagues at the University of Chicago have determined within 10 per cent that the quartz in a sample of granite contains only one part of uranium in 10 million. Comparable precision has been obtained in measuring other trace elements.



SPECTRA OF LEAD from various sources show differences in isotopic content. Thorium decays to lead 208 (*top*); uranium 238 ends as lead 206; uranium 235 as lead 207 (*center*); natural lead (*bottom*) is a mixture of isotopes, which may vary from one deposit to another by as much as the shaded area in each bar, but which average to the same atomic weight.

ONE OF THE most interesting uses of the mass spectrometer has been in reckoning the age of the earth. The method involves measuring the isotopic abundances of lead, the product of the breakdown of radioactive uranium and thorium, in the earth's rocks. In the long course of time uranium 238 decays to the lead isotope 206, and uranium 235 to lead 207. Thorium decays to lead 208. The rates at which these transformations take place are accurately known. Thus by making a chemical analysis of the amounts of uranium, thorium and lead in a sample of mineral, and determining the relative amounts of the three isotopes of lead, one can make three independent calculations of the age of the mineral. Once the ages of the uranium and thorium minerals are calculated, it becomes possible to estimate accurately the ages of the deposits in which they lay and thereby to set up an age scale for the various geological eras. The oldest minerals found so far have an age somewhat over two billion years. Thus the earth must be at least this old.

The problem is complicated by the fact that the mineral may contain some "ordinary" lead; that is, lead which was lead all along and not formed by the breakdown of uranium or thorium. The mass spectrometer, however, can distinguish between primeval lead and the kind due to radioactive decay, known as radiogenic lead. In the early part of this century many samples of ordinary lead as well as radiogenic lead were carefully studied, principally by the late T. W. Richards of Harvard University and his successor, G. P. Baxter, and their students. Their samples of ordinary lead were always found to have precisely the same atomic weight. But in 1937 I analyzed the same samples with a mass spectrometer and learned that nature had carefully hidden a secret. Although the average weight of the lead was the same in all the samples, the accurate spectrometric analysis showed that the relative abundances of the lead isotopes varied widely from sample to sample. How it came about that the isotopes collected in such proportions that the average weight was always the same is a mystery. The effect apparently has to do with the early history of the lead—its

proximity to uranium and thorium—before it was laid down in the mineral in which it is now found. The problem requires far more investigation. Calculations made from the data so far available have led the eminent geologist Arthur Holmes of the University of Edinburgh to suggest that the actual age of the earth is close to 3.3 billion years.

The mass spectrometer has many other applications to problems in geophysics and geochemistry. One of the most engaging is employed by Harold Urey and associates at the University of Chicago in determining from the fossil shells of marine animals the temperature of the oceans in which they lived millions of years ago. Urey and his associates have shown that when calcium carbonate, the material forming the shells, is crystallized slowly in water, the ratio of rare oxygen 18 to common oxygen 16 in the carbonate will depend slightly upon the temperature of the water. The effect is very small: a change in temperature of one degree centigrade changes the ratio by only .02 per cent. Since oxygen normally contains only one part of O-18 to 500 parts of O-16, this change affects the atomic weight of oxygen by less than one 10-millionth of a unit of atomic weight. Nevertheless Urey and his colleagues, with the aid of a mass spectrometer, have found measurable isotopic differences in the oxygen extracted from fossil shells and have been able to calculate the temperatures of the oceans in which the animals lived —a valuable bit of evidence in reconstructing the early history of the earth. The technique has been perfected to the point where, by examining successive layers of an animal's shell, one can even determine seasonal variations in temperature and in some instances the time of year the animal died!

Other workers have investigated by mass spectrometry variations in the isotopic abundances of certain other elements, including boron, sulfur and helium. Several years ago one of my students, L. T. Aldrich, and I measured the abundance of the rare isotope helium 3 in various sources of helium and found that it ranged from 5 to 2,000 parts per 100 million—a 400-fold variation! Abundant helium 4 is a by-product of the radioactive decay of uranium and thorium, while helium 3 is the decay product of unstable hydrogen 3 (tritium). Tritium, in turn, is formed in various ways, including cosmic-ray bombardment. Hence the problem of explaining the variations is extremely complex.

TO THE MEN who developed the mass spectrometer—Thomson, Aston, Dempster, the late John T. Tate of Minnesota and others—workers in many fields today are much indebted. The specialists who have put the instrument to "practical" use already include petroleum chemists, atomic fuel producers, biologists, geologists—and the list will certainly grow far longer.

The Author

ALFRED O. C. NIER, chairman of the department of physics at the University of Minnesota, built his first mass spectrometer as a graduate student at Minnesota. "I found that I had in my hands," he says, "the best instrument then in existence for studying isotopes." In 1935, a year before getting his doctorate, he found the extremely rare isotope of potassium, K-40. While Nier was at Harvard the following year on a National Research Council fellowship, his work attracted the attention of G. P. Baxter, the venerable authority on atomic weights. Baxter prepared special compounds for him, including uranium tetrachloride, with which Nier determined for the first time the relative abundance of isotopes U-235 and U-238. When he returned to Minnesota in 1938, it wasn't long before he had to take up the uranium problem again. It was Nier who, by separating pure U-235 and U-238 with the mass spectrometer, made it possible to settle the question as to which was the fissionable isotope. He worked during the war with the Manhattan District and the Kellex Corporation, builder of the U-235 gaseous diffusion plant at Oak Ridge.

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